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Preparation and sizing mechanisms of neutral rosin size II: functions of rosin derivatives on sizing efficiency

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Abstract Four rosin derivatives, including rosin esters and rosinamides, were synthesized and used to prepare neutral rosin sizes. Their effects during sizing are discussed in detail. Compared to natural rosin, the rosin derivatives had nearly no effect on sizing even at high retention levels in paper. However, the rosin derivatives in the rosin sizes improved the stability of the emulsion size particles, and there was good correlation between the sizing effect and the stability of the emulsion sizes under neutral to alkaline conditions. On the other hand, the structure of the rosin derivatives significantly influenced the stability and sizing effect of the neutral rosin sizes. In particular, for glycerin rosin ester–rosin sizes, the emulsion stability and sizing effect increased with an increasing proportion of dirosinate, among the glycerin rosin esters. Consequently, it was suggested that the rosin derivatives hardly contribute to the sizing performance of paper but predominantly function to stabilize the neutral rosin size particles, thereby improving the efficiency of the size under neutral to alkaline sizing conditions. Also it was supposed that glycerol dirosinate in the neutral rosin size would probably enable formation of a more stable particle structure to prevent the destructive action of the OH^- ion.

Key words Rosin derivatives · Neutral rosin sizes · Neutral to alkaline sizing · Glycerol dirosinate

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Introduction

Sizing of paper with rosin is a traditional chemical process in modern papermaking. Since its discovery in 1804, rosin sizing has been the subject of extensive research and product improvement.[1] Rosin sizes have undergone changes or modification from rosin soap to colloidal rosin, anionic or cationic dispersed rosin emulsion size, and neutral rosin size.[2–6] During conventional acidic rosin sizing, the yellowing and deterioration of acidic paper are caused by the introduction of alum, and the acidity leads to paper embrittlement and loss of strength.[7] Moreover, rosin soap size is believed to react easily with calcium ions in paper stock water with high hardness to form precipitated calcium rosinate particles with negative surface charges; those particles are difficult to attach to the fiber surface.[8–9] Once adsorbed on pulp fiber surfaces, size emulsion particles with excess free rosin acid are easily decomposed and dissociated from fibers by the action of OH^-.[10] Therefore, the development of some new types of rosin size that need less alum as a retention aid and exhibit good sizing under neutral to alkaline conditions has been an interesting project.

Many studies on the modification of natural rosin and improvement of size emulsion stability at higher pH values have been carried out in recent years. As the most popular derivative of rosin, glycerin rosin ester was reported to be suitable for the preparation of a neutral rosin size.[11–13] As modified products of rosin, mixtures of rosinamides and rosin have been proposed for making neutral rosin size.[14] Cationic dispersed rosin size, which is called a self-retainable size, was also reported.[15–18] Tahara et al. described a new neutral sizing agent prepared from petroleum resin emulsified with a cationic surfactant. It can be used for paper sizing without alum under alkaline conditions.[19] Although many studies have been done, there are still few neutral rosin sizes successfully used for practical neutral to alkaline paper sizing. In particular, the mechanisms of neutral rosin sizing are not clear, and the functions of rosin esters or rosinamides in neutral rosin sizes are disputable.

The objectives of this study were to prepare new neutral rosin sizes and investigate the effects of rosin derivatives on the properties of the rosin sizes and on paper sizing. For this research, various rosin esters and rosinamides were synthsized and used alone or with rosin to prepare emulsion sizes, and their sizing features were compared. The effects of the structures of rosin derivatives and the variation in glycerin rosin ester components on the sizing effect were investigated in terms of the stability of the size emulsions in the presence of pH changes and the sizing degrees of paper sheets prepared under different conditions.

Materials and methods

Materials

The pulp used to make handsheets was hardwood bleached kraft pulp (HBKP), which was beaten to 390ml of Canadian Standard Freeness with a TAPPI standard beater. Gum rosin was used as a typical rosin material, and all other chemicals used for preparing rosin ester and rosinamide were analytical reagents. A 10% tetramethylammonium hydroxide solution in water (TMAH) was employed as the methylation reagent for pyrolysis gas chromatography (Py-GC).

Synthesis and analysis of various rosin derivatives

N-Cyclohexyl rosinamide and benzyl rosinate were synthesized as reported previously.[20,21] Glycerol rosinate was prepared using the following procedures. Gum rosin 30.2g (0.1mol) charged in a three-neck reaction vessel was heated to around 180°C, and 0.2% zinc oxide on rosin was added as catalyst. After 5min 3.5g (0.038mol) of glycerol was added. To prevent vaporization of the glycerol, the reaction was carried out with a reflux condenser. The esterification reaction was continued for 3–6 hours at about 250°–290°C. Finally, the condenser was disconnected from the vessel, which was then allowed to stand for 30min to vaporize the water produced and the unreacted glycerol. For the synthesis of *N,N*-diethanol rosinamide, 30.2g of gum rosin was heated to about 150°C; then 11.6g (0.11mol) of diethanolamine was added to the system. This reaction can be divided into two steps. In the first step, rosin was reacted with diethanolamine for about 2h at about 160°C to convert it into the ammonium salt. Second, a dehydrating reaction was carried out for 1.5–3.0h at 200°–230°C.

The reaction was monitored by thin-layer chromatography (TLC) (Kieselgel 60 F254, Merck) using a mixtures of ethyl acetate, heptane, and methanol (4:4:1, v/v) as a developing solvent, and the acidity of the final products was measured according to TAPPI method T 621 cm-82. FT-IR, GC-MS, and FAB-MS were employed for qualitative analysis of the reaction products; and Jasco high performance liquid chromatography (HPLC), with a column of DEVELOSIL-60-3 using a mixture of ethyl acetate, heptane, and methanol (4:4:1 v/v) as an eluting solvent, was used to quantitate the components.

Preparation of rosin size emulsions

An inversion process at high temperature under atmospheric pressure was used to prepare the size emulsions. Natural rosin, the rosin derivative, or the mixture was heated to around 150°C and converted to the water-in-oil (W/O) phase by adding a small amount of emulsifier solution, the W/O phase was then changed to the stable oil-in-water (O/W) phase by rapid addition of hot water with vigorous stirring so the resin particles were evenly dispersed in water. For this purpose, a certain amount of a suitable emulsifier must be used. In this research, 6.5% on the resin solids of emulsifier RB-330 (Daochuang Chemical. Co., China) was used for emulsification, with the exception of 10% for the tests in Table 1 (below) because of the difficulty of emulsification. Various size emulsions were obtained containing 20%–30% solids and with average particle diameter of 0.35–0.45μm. The prepared size emulsion was diluted to 2% prior to use.

Measurement of particle size and turbidity of rosin size emulsions

The estimation of particle size distribution and average diameter of various rosin size emulsions was carried out on a Shimadzu SALD-3000 laser diffraction particle size analyzer. The turbidity of the size emulsions at various pH levels was measured with a DRT 100 turbidity instrument (HF Instruments, USA). The concentration of size emulsions for the measurement of both particle size and turbidity was 0.01%, and the time from pH adjustment to turbidity measurement was 15min for experiments on size emulsion stability.

Sizing and paper preparation

To a 1.2% pulp suspension, dilute NaOH or HCl solution was added to adjust the pH to the desired value, following which certain amounts of aluminum sulfate solution and then the size emulsion were added. Once again the pH of this paper stock was adjusted to the prescribed value with dilute NaOH or HCl solution, and the paper stock was stirred for 3min. Handsheets with a basis weight of 60g/m^2 were prepared according to TAPPI method T 205 om-88. Formed and wet-pressed handsheets were dried in an oven at 105°C for 10min and then conditioned at 20°C and 65% relative humidity for more than 24h.

Determination of sizing degree and size content of paper sheets

Each of the sized paper sheets was divided into two parts. One part was used to test the sizing degree with the Stöckigt method (JIS P8122), and the other part was used to determine size content by the Py-GC method.[22] For Py-GC analysis, each paper specimen was milled into fine powder prior to the test and weighed to exactly 0.5 mg with a microbalance. The pyrolysis temperature was set at 450°C, and 4 μl of TMAH was used as the methylation reagent.

Results and discussion

Structure and sizing effect of rosin derivatives

Understanding whether rosin esters or rosinamides have a sizing effect on paper is necessary for us to investigate the sizing mechanisms of neutral rosin sizes. In this study, four rosin derivatives, including *N,N*-diethanol rosinamide (DRA), *N*-cyclohexyl rosinamide (CRA), glycerin rosin ester (GRE), and benzyl rosin ester (BRE), were studied for sizing compared with natural rosin (NR). These four rosin derivatives and natural rosin were made into emulsion sizes using 10% emulsifier RB-330, as it is difficult to emulsify rosin derivatives. They were used to size paper via dip sizing and internal sizing. For dip sizing, paper sheets of 60 g/m^2 basis weight pretreated with 1% aluminum sulfate at pH 5 were dipped in 50 ml of 2% size emulsion for 60 s. For internal sizing, paper sheets were sized with 1% size and 1% aluminum sulfate at pH 5. The results were shown in Table 1.

According to the data in Table 1, the sizing effect of the resins used does not correspond with their glass transition point (Tg, determined according to JIS K 7121) but mainly depends on the structure – whether it contains a carboxyl group. Ito et al. reported that paper sized with a size emulsion consisting of only rosin ester had a low degree of sizing.[6] Our experimental results indicated that rosin esters and rosinamides had nearly no sizing effect, as even the size content in paper is higher with dip sizing.

It is well known that good sizing of paper with rosin sizes depends on the following three key factors.[23–25] (1) Sufficient rosin size particles are retained on the paper; (2) the sizes are evenly distributed; and (3) the size components are well oriented on the surface of fibers. If any one of these conditions is not met, good sizing is not obtained. As shown in Table 1, none of the rosin derivatives used brought about sizing of any degree during either dip sizing or internal sizing, whereas the natural rosin produced good sizing. This means that the carboxyl group of the rosin is important for the sizing performance. In the case of natural rosin, carboxyl groups can react with aluminum cations formed on the fiber surface so rosin particles are easily retained, and rosin molecules would be oriented well such that the tricyclic alkyl – a highly hydrophobic tail – is oriented away from the fiber surface.

In contrast, rosin esters and rosinamides, despite their higher hydrophobicity than that of rosin, were difficult to retain by aluminum cations at the wet-end and could not be oriented well at the dry-end because of blockage of the carboxyl group, which has reactivity with aluminum. Hence, the distribution of size particles on the surface of fibers are probably uneven, and the relatively strong hydrophobic tail is not easily oriented away from the fiber surface to produce good sizing. As shown in Table 1, the facts that (1) there is lower retention of rosin esters and rosinamides compared to rosin acid during internal sizing and (2) there is no sizing even at a higher size content during dip sizing support the above hypothesis. Therefore, it is proposed that rosin esters and rosinamides contribute little to the sizing of paper sized by neutral rosin sizes.

Differences in effectiveness of rosin sizes containing different rosin derivatives

As mentioned above, rosin esters and rosinamides have little effect on sizing. However, it is a fact that neutral rosin size containing suitable rosin ester or rosinamide exhibits quite good sizing under neutral to alkaline conditions. Then what role does the rosin ester or rosinamide play in the rosin size and sizing? It was considered traditionally that acid rosin sizes were unstable to the calcium ion in hard water or in the system loaded with alkaline filler calcium carbonate, and that the use of rosin esters or rosinamides might avoid the influence of calcium ion. Our results with particle size distribution measurements (unpublished work), however, showed that the reaction rate of acid rosin emulsion size particles with calcium ion in a 0.1% calcium chloride solution was slow, and the formed particles were different from the flocculates of calcium rosinate. These results suggested that the effect of calcium ions may be not a main problem regarding the emulsion type of rosin sizes. Hence it is desirable to discuss further the functions of rosin derivatives in neutral rosin sizes and sizing.

Kitaoka et al.[10] stated that light transmittance of the acid rosin size emulsion sharply increased after addition of

Table 1. Characteristics and sizing features of rosin and various rosin derivatives

Resins	Structural feature	Acid number	Tg (°C) (DSC)	Size content (mg/g paper)		Sizing degree (s)	
				Dip sizing	Internal sizing	Dip sizing	Internal sizing
NR	–COOH	168	37.5	10.3	4.8	22	40
DRA	–CON, –OH	8	39.4	8.1	2.3	0.5	0
CRA	–CON	6	44.4	7.8	2.1	1	0
GRE	–COOR, –OH	5	59.5	7.6	2.5	1	1
BRE	–COOR	2	Liquid	8.9	2.8	2	1

NR, natural rosin; DRA, *N,N*-diethanol rosinamide; CRA, *N*-cyclohexyl rosinamide; GRE, glycerin rosin ester; BRE, benzyl rosin ester; Tg, glass transition point; DSC, differential scanning calorimetry

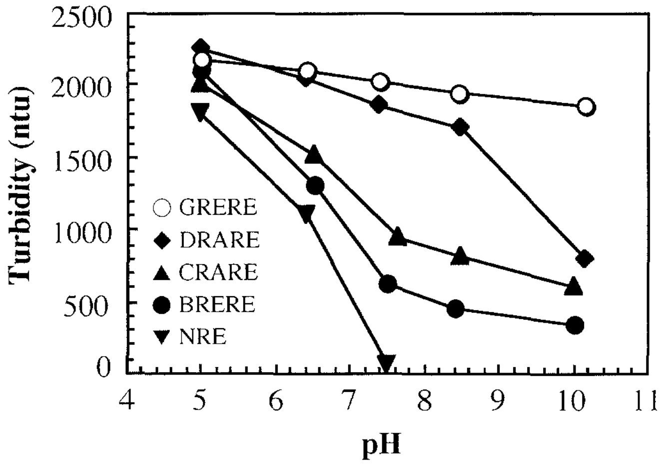

Fig. 1. Turbidity of various 0.01% size emulsions at different pH levels. GRERE, glycerin rosin ester–rosin emulsion; DRARE, *N,N*-diethanol rosinamide–rosin emulsion; CRARE, *N*-cyclohexyl rosinamide–rosin emulsion; BRERE, benzyl rosin ester–rosin emulsion; NRE, natural rosin emulsion

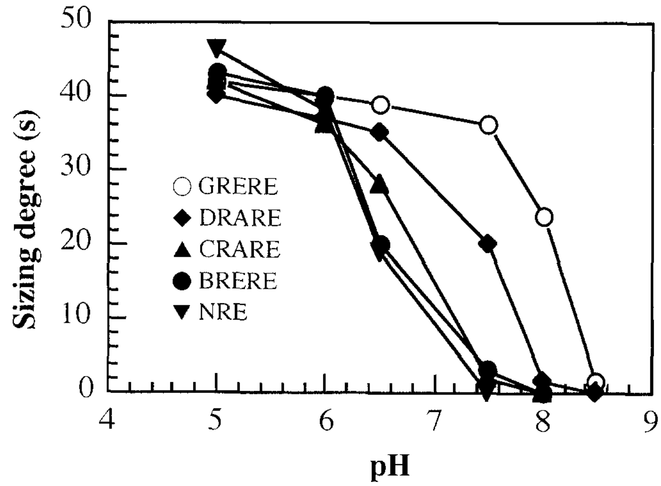

Fig. 2. Sizing degrees of paper sheets sized with 1% aluminum sulfate and various 1% sizes at different pH levels. See Fig. 1 for abbreviations

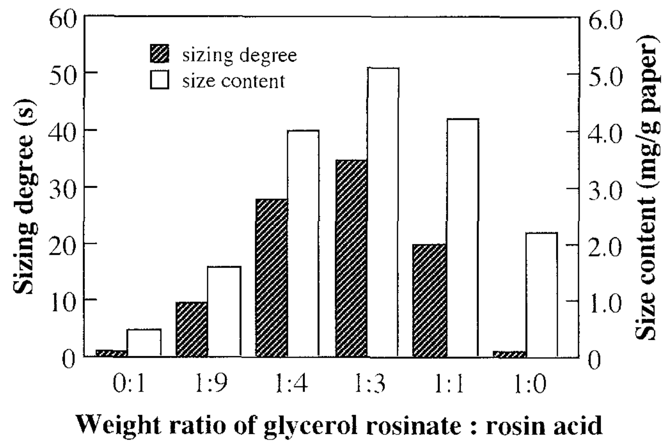

Fig. 3. Relation between sizing effect and the glycerol rosinate/rosin weight ratios in the size. Paper sheets were sized with 1% aluminum sulfate and 1% size at pH 7.5

sodium hydroxide, and that rosin size particles once retained on the fiber surface were likely dissociated as a function of OH^-. In the present research, we attempted to better understand the functions of rosin derivatives by investigating the relation between the sizing effect and the stability of various rosin-based size emulsions at different pH values. For this purpose, four emulsions consisting of rosin derivative and natural rosin (weight ratio 1:3), including glycerin rosin ester–rosin emulsion (GRERE), *N,N*-diethanol rosinamide–rosin emulsion (DRARE), *N*-cyclohexyl rosinamide–rosin emulsion (CRARE), and benzyl rosin ester–rosin emulsion (BRERE), were compared with natural rosin emulsion (NRE). An emulsion rosin size is a suspension in which rosin particles are dispersed in water; its turbidity varies when the number of rosin particles in the emulsion are changed. Stable turbidity is related to the free rosin acid in the size; and the dissociation of rosin acids results in diminished turbidity.[26] Thus, we can estimate the stability of the emulsion rosin size by the variation in its turbidity at different pH levels. As illustrated in Fig. 1, it is apparent that the stability of the various rosin sizes was considerably different when the pH increased. Compared to NRE, in which the turbidity sharply decreased and the emulsion particles were fully dissolved when the pH rose to 7.5, the turbidity of rosin derivative–rosin size emulsions was seen at different degrees up to pH 10. It is also clear that the ability of rosin derivatives to improve the stability of the rosin size corresponds to their structure. GRE and DRA, with a hydroxy group in their molecular structure (Table 1), are relatively good; and GRE is considered to be the most efficient.

As shown in Fig. 2, the results indicated that the sizing effects of the prepared sizes were quite different from one another. Although NRE gave a higher degree of sizing than the others at pH 5, its sizing effect sharply decreased as the pH rose and disappeared at 7.5. The sizing effects of CRARE and BRERE were better than that of NRE at pH 6.5, but they had no sizing effect at neutral to alkaline conditions. On the other hand, GRERE and DRARE induced a higher degree of sizing at pH 7.5, and GRERE in particular produced good sizing even up to pH 8. According to the results shown in Figs. 1 and 2, there was a good correlation between the sizing effect and the stability of the rosin sizes under sizing conditions. These results suggest that (1) the stability of rosin sizes to the addition of alkali solution is important for their neutral to alkaline sizing, (2) the addition of suitable rosin derivate to the rosin size makes it possible to improve the size's emulsion stability; and (3) rosin derivatives having a hydroxy group in the molecule are probably more efficient for the preparation of neutral rosin size.

In addition to the structure of the rosin derivatives, the proportion of derivative in the mixture affects the sizing effect of the neutral rosin size. Figures 3 and 4 show the influence of the glycerol rosinate/rosin weight ratio on the sizing effect and the stability of the size, respectively. As

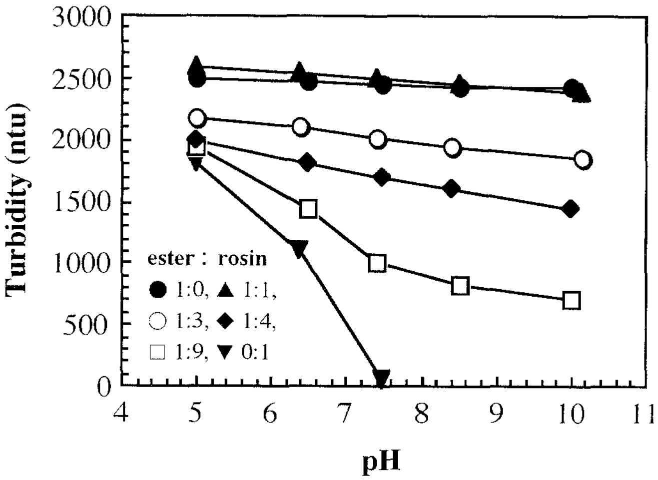

Fig. 4. Turbidity of size emulsions with different glycerol rosinate/rosin weight ratios in the size at different pH levels

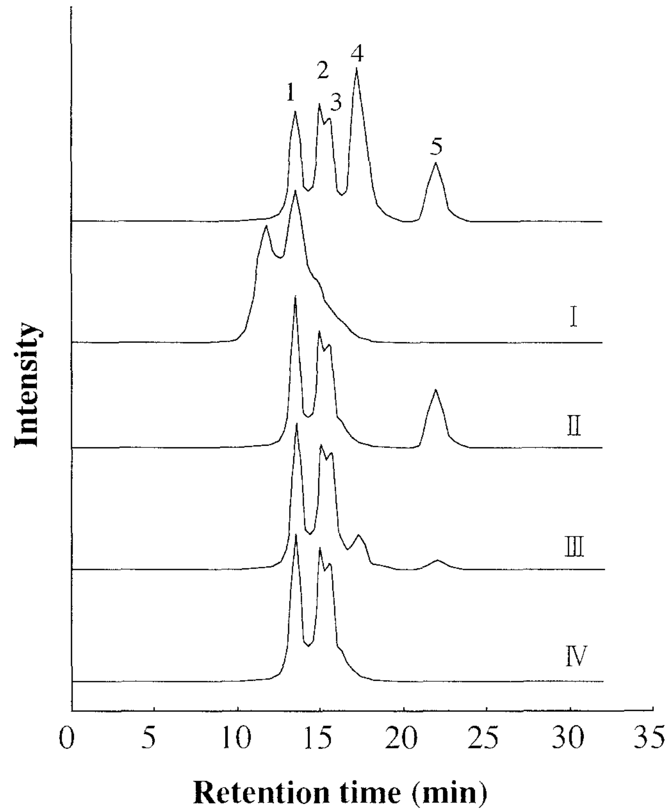

Fig. 5. High-performance liquid chromatography (HPLC) patterns of glycerol rosinates produced under conditions I–IV, shown in Table 2. Peaks were assigned for glycerol trirosinate (*1*), glycerol dirosinate (*2* and *3*, isomer), rosin acids (*4*), and glycerol monorosinate (*5*)

illustrated in Fig. 3, the emulsion size without the rosin ester had nearly no sizing because there was little size retained; the emulsion size with rosin ester alone also produced little sizing despite the relatively higher size content. The sizing degree and size content of paper gradually increased with an increasing rosin ester/rosin weight ratio in the size up to 1:3 but declined when the weight ratio was greater than that. The results in Fig. 4 illustrate that the increasing amount of rosin ester in the size achieves higher stability of the rosin size emulsion at higher pH values. However, large quantities of a rosin derivative in the rosin size brought about only higher stability, rather than sizing degree, probably due to a decrease in the effective sizing component – rosin acids – implying that rosin derivatives do not contribute to the sizing degree of the paper.

Influence of components in glycerol rosinates on sizing

In our experiments it was found that there were the differences in the sizing of paper with the two neutral rosin sizes containing the same amount of glycerol rosinate products but different ester components in the glycerol rosinate products. For further study, four glycerol rosinate products were obtained by changing the reaction temperature, reaction time, and rosin/glycerin molar ratio. They were then analyzed by HPLC to distinguish the effect of the glycerin rosin ester components. The reaction conditions for the ester synthesis are shown in Table 2 and the analytical results in Fig. 5. Because glycerin is a trivalent alcohol, the esterification reaction of rosin with glycerin produces three glycerol rosinates: glycerol monorosinate, glycerol dirosinate, and glycerol trirosinate. In Fig. 5, peaks were assigned for trirosinate (1), dirosinate (2,3 isomer), rosin acids (4), and monorosinate (5) depending on the difference in their polarity. As shown in Table 2 and Fig. 5, the composition of rosinates in the products varied with the changing reaction conditions.

Table 2. Reaction conditions for various glycerol rosinate samples

Sample no.	Temperature (°C)	Time (hr)	Molar ratio of –COOH to –OH
I	290	6	1:1
II	250	4	1:2
III	270	5	2:3
IV	260	4.5	1:1

Figure 6 shows the results of stability and sizing effects of the glycerol rosinate–rosin sizes, in which the rosin/glycerol rosinate weight ratio of samples I, II, III, and IV (Fig. 5) was 3:1. The remained turbidities of 0.01% size emulsions when altering the pH from 5 to 10 were measured to evaluate the stability of sizes, and the sizing experiments were carried out for papers sized with 1% size and aluminum sulfate at pH 7.5. As illustrated in Fig. 6, it is apparent that the stability and sizing effect of the glycerol rosinate–rosin sizes were significantly influenced by the glycerol rosinate component. The rosin sizes containing ester sample III or IV, which was rich in dirosinate and almost without monorosinate, had better stability and sizing efficiency, whereas the rosin sizes containing ester sample I or II, without dirosinate or with a large amount of monorosinate, had less stability and poor sizing. The results suggested that

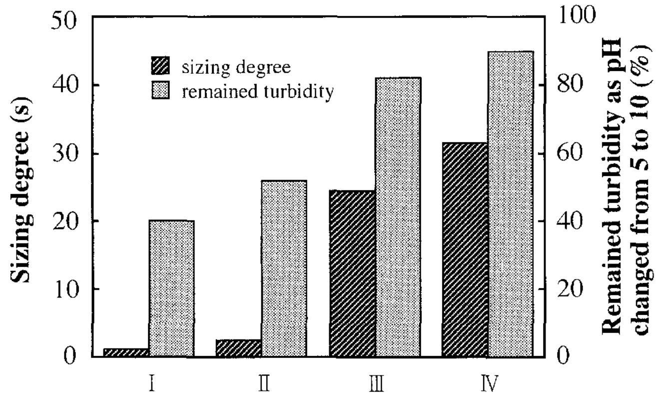

Fig. 6. Influence of ester components on the stability and sizing effect of a glycerin rosin ester–rosin size

glycerol dirosinate predominantly contributed to the improved stability and sizing effect of the glycerol rosinate–rosin size under neutral to alkaline conditions. It is probably due to the formation of stable size particles, which are not easily dissociated by the addition of alkali as a function of glycerol dirosinate during the emulsifying process.

Conclusions

Four rosin derivatives with different structures were synthesized and used for the preparation of neutral rosin emulsion sizes, which were employed in sizing paper to elucidate the functions of the rosin derivatives for neutral to alkaline rosin sizing. The results with rosin derivatives compared to those with rosin acid indicated that rosin esters or rosinamides themselves had nearly no sizing effect, whereas there was a high degree of sizing of paper with rosin acid. The variation in the turbidity of the rosin size emulsions as the pH changed revealed that the most important function of the rosin derivative in the neutral rosin size is to improve the stability of the rosin size emulsion particles under neutral to alkaline conditions. On the other hand, it was shown that, the variation in rosin ester components significantly influenced the size features of the glycerin rosin ester–rosin size; and the stability and sizing effect of the glycerin rosin ester–rosin sizes increased with an increasing proportion of glycerol dirosinate. This finding implies that glycerol dirosinate probably plays an important role in the formation of stable rosin size particles.

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